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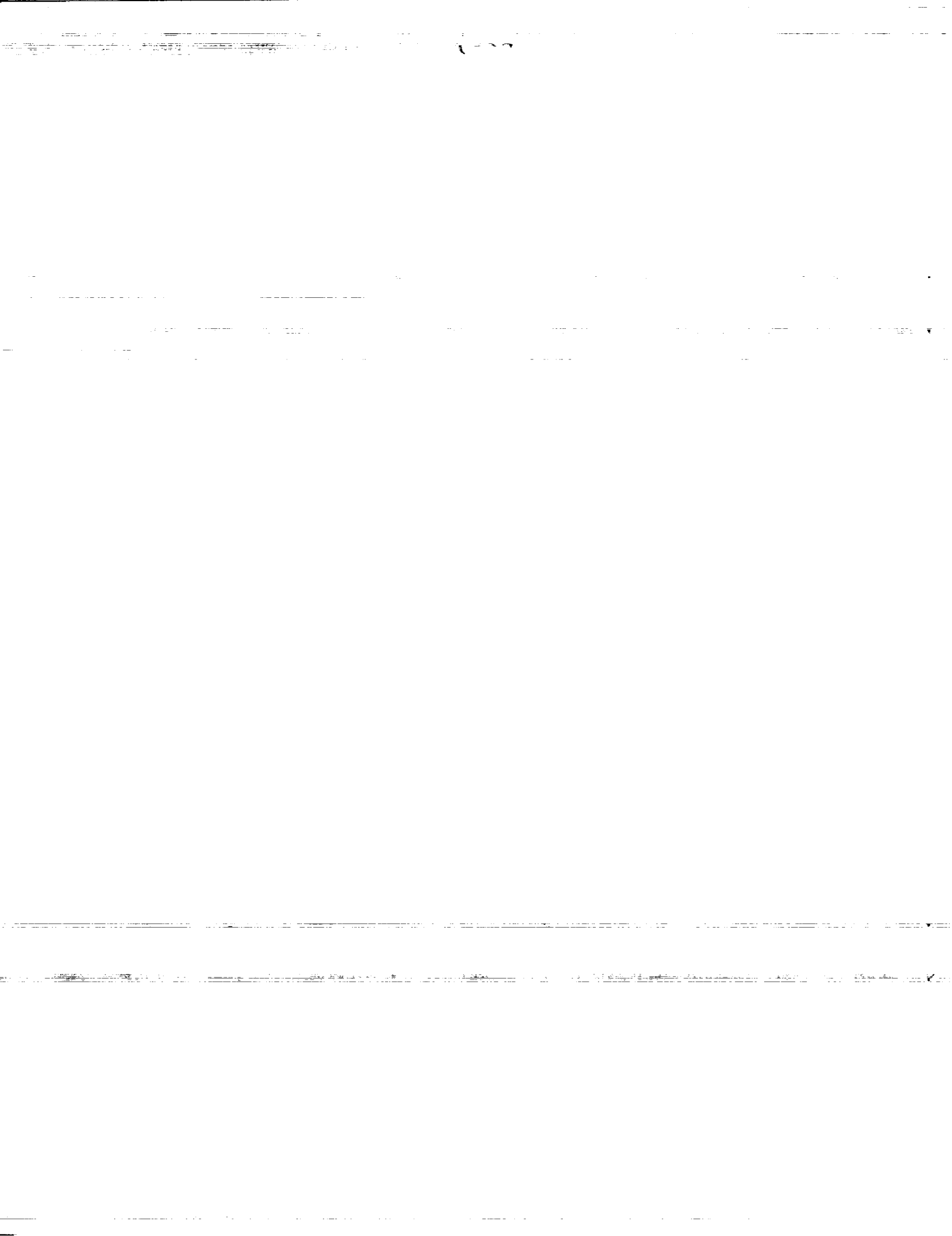
Prepared for the
Fall Meeting of the Materials Research Society
Boston, Massachusetts, November 26—December 1, 1990

(NASA-TM-103666) REACTIVITY OF π -COMPLEXES
OF Ti, V, AND Nb TOWARDS DITHIOACETIC ACID:
SYNTHESIS AND STRUCTURE OF NOVEL METAL
SULFUR-CONTAINING COMPLEXES (NASA) 6 p

N91-19256

Unclass
CSCL 07D G3/25 0001677

NASA



REACTIVITY OF π -COMPLEXES OF Ti, V, AND Nb TOWARDS DITHIOACETIC ACID: SYNTHESIS AND STRUCTURE OF NOVEL METAL SULFUR-CONTAINING COMPLEXES

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INTRODUCTION

As the price of crude oil rises, the use of feedstocks with increased levels of sulfur and metals will increase [1]. In order to use these resources economically and with minimal environmental damage, it is important to understand processes such as hydrodesulfurization (HDS) and hydrodemetallation (HDM) catalysis [2]. A Co-promoted molybdenum sulfide (Ni or W are sometimes substituted for Co and Mo) on γ -alumina catalyst is the industry standard for metal and sulfur removal under H_2 ; HDM is often part of the HDS process [3]. A periodic effect on the activity of metal sulfides for HDS was demonstrated by Pecoraro and Chianelli [4]. Maximum activity was observed for second- and third-row platinum group metal sulfides: RuS_2 , OsS_2 , Rh_2S_3 , and IrS_2 were shown to have 20 to 40 times the activity of MoS_2 [4]. Early transition metal sulfides, on the other hand, have minimal HDS activity [4]; vanadium, for example, can actually *inhibit* catalytic activity [1].

The study of simple inorganic model systems can also enhance an understanding of catalytic processes. Detailed knowledge of relevant systems can be gained from structural and spectroscopic studies of sulfur-containing metal compounds. A further motivation for this chemistry is the possible invention of novel precursors for solid state materials [5], with potentially improved properties. In light of the above discussion and the biological relevance of iron- and molybdenum-containing metal sulfur clusters [6], it is not surprising that many model system [7] and catalytic studies [8] focus on the chemistry of compounds of group 6 through 12 metals. However, while there is tremendous activity and interest in the chemistry of metal complexes with sulfur-containing ligands [9-11], this interest generally does not extend to the electron deficient transition metals, particularly vanadium. Since the vanadium content of some crude oils approaches 1000 ppm [1] it is important to learn more about vanadium sulfur chemistry. Our interest in early transition metal and sulfur chemistry [12] led us to explore the reactivity of V, Nb, and Ti sandwich compounds with an organic sulfur source, dithioacetic acid [13]. The following discusses some of our recent work as it relates to desulfurization of dithioacetic acid and new preparative routes to metal sulfide precursors.

EXPERIMENTAL

All manipulations of moisture and air-sensitive materials were done under an inert atmosphere by standard Schlenk techniques on a double-manifold vacuum line or in a Vacuum Atmospheres Co. glovebox equipped with a HE-493 dri-train. Solvents were freshly distilled from benzophenone ketyl prior to use. The metal sandwich compounds and CH_3CSSH were synthesized as described in [13]. NMR spectra were recorded on a Bruker AC300F or a Varian FT-80A. Infrared spectra were recorded on a Perkin-Elmer 599B spectrophotometer. Electron impact mass spectra were recorded on a Finnigan TSQ-45 mass spectrometer. All single-crystal x-ray analyses, except the divanadium complex, were performed on an Enraf-Nonius CAD-4 diffractometer.

RESULTS AND DISCUSSION

$[(\eta^5\text{-C}_5\text{H}_5)\text{Ti}(\eta^7\text{-C}_7\text{H}_7)]$ reacts with excess CH_3CSSH in toluene at 25°C for 3 days to produce $[(\eta^5\text{-C}_5\text{H}_5)\text{Ti}(\text{S}_2\text{CCH}_3)_3]$, 1, in 83 % yield. Gas chromatography/ mass spectral (GC/MS) analysis of the reaction solution showed the presence of 1,3,5-cycloheptatriene. Light yellow prismatic crystals were grown by layering a toluene solution of 1 with hexanes [14]. $[(\eta^5\text{-C}_5\text{H}_5)\text{Nb}(\eta^7\text{-C}_7\text{H}_7)]$ reacts with excess CH_3CSSH in diethyl ether for 4 days to produce $[(\eta^5\text{-C}_5\text{H}_5)\text{Nb}(\text{S}_2\text{CCH}_3)_2(\eta^2\text{-S}_2)]$, 2, in 83 % yield. GC/MS of the reaction solution showed the presence of cycloheptatrienyl dimer. Red black prismatic crystals were grown by layering a diethyl ether/toluene solution of 2 with heptane [15]. $(\eta^6\text{-C}_6\text{H}_6)_2\text{V}$ reacts with excess CH_3CSSH in toluene at 25°C for 4 days to produce $[(\text{CH}_3\text{CS}_2)_2\text{V}(\mu\text{-}\eta^2\text{-S}_2)_2\text{V}(\text{S}_2\text{CCH}_3)_2]$, 3, in yields up to 62 %. Brown crystals were grown by layering a benzene solution of 3 with heptane [16]. $(\eta^5\text{-C}_5\text{H}_5)_2\text{V}$ reacts with excess CH_3CSSH in THF-toluene at 25°C for 4 days to produce $[(\eta^5\text{-C}_5\text{H}_5)_4\text{V}_4(\mu_3\text{-S})_4]$, 4, in yields up to 47 %. Dark purple cubic crystals were grown by layering a toluene solution of 4 with heptane [17]. ORTEP structures of 1, 2, 3 and 4 are shown in figure 1.

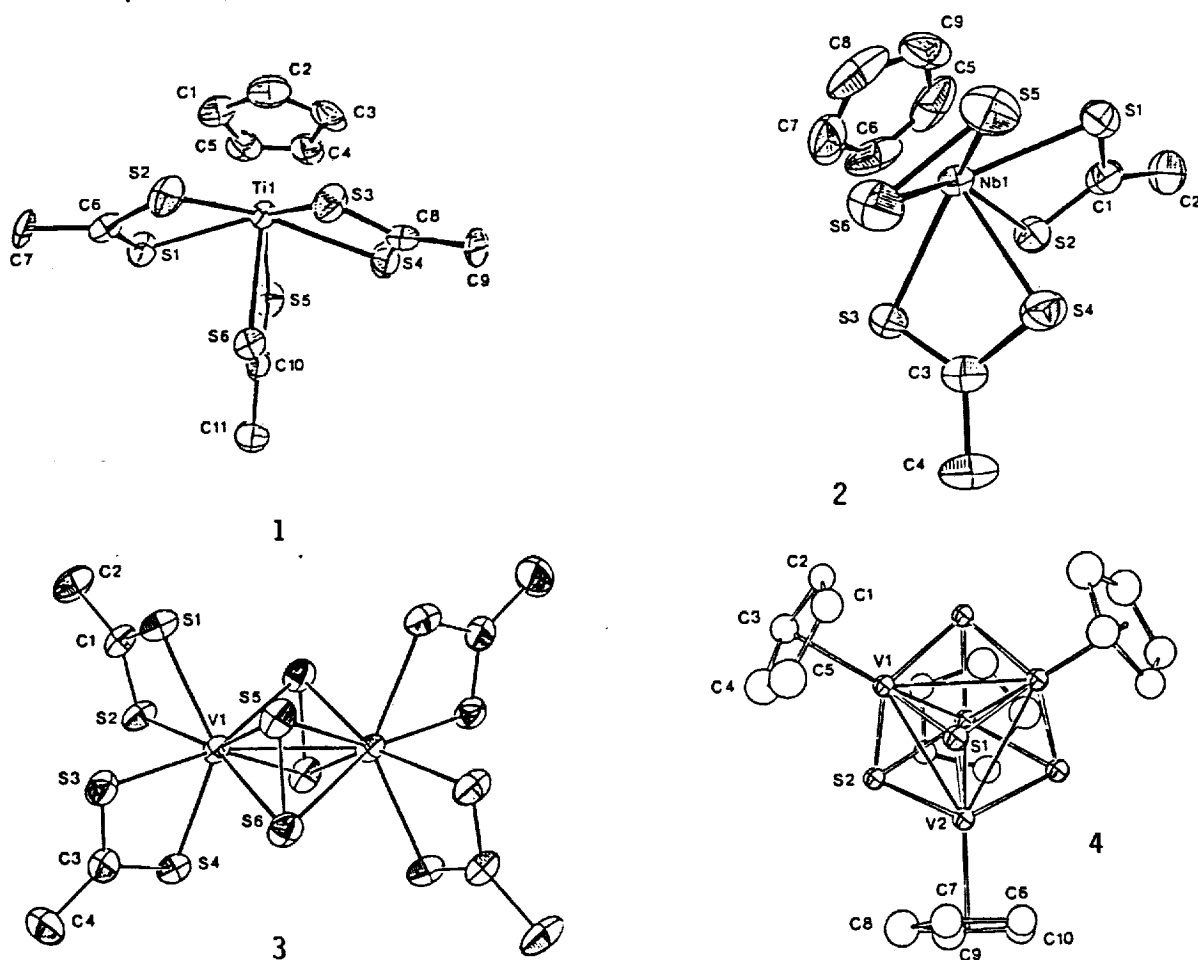


Figure 1. ORTEP drawings of 1, 2, 3, and 4 also define the labelling scheme. The thermal ellipsoids enclose 50% of electron density.

Magnetic susceptibility, NMR and structural data are consistent with a d^0 electronic structure for 1 and 2. Both complexes have retained a cyclopentadienyl ring in the coordination sphere. Several differences between 1 and 2 are apparent when the two complexes are compared. Most important is the side-on chelating disulfide that is formed in the course of the synthesis of 2 but not in 1. Both complexes have pentagonal bipyramidal structure, but 2 is distorted by the small angle of $\text{S}(5)\text{-Nb-S}(6)$ of 48° due to the side-on bonding of the disulfide.

Complex 1 is the first examples of an organometallic Ti dithioacetate complex; 2 is the first example of a Nb dithioacetate. Analysis of the cycloheptatriene fragments imply that different mechanisms are operating for Ti and Nb complex formation. An $\eta^7 \rightarrow \eta^1$ isomerization followed by protonation results in the formation of 1,3,5-cycloheptatriene; the dithioacetate replacing the η^1 -C₇H₇ ligand to yield a Ti(IV) complex that cannot be oxidized further after the tris dithioacetate is formed. The by-product cycloheptatrienyl dimer in 2 implies that desulfurization promotes oxidation of tetravalent Nb and rapid loss of C₇H₇, resulting in radical coupling. The lack of any further reaction of Ti in 1 illustrates the lack of HDS activity in group IV sulfides [1,4]: the stability of Ti(IV)-sulfur bonds.

Magnetic susceptibility and structural data is consistent with bonding between vanadium atoms in both 3 and 4. In 3, a V-V distance of 2.800 Å, is consistent with a single bond; the compound is diamagnetic as expected for a d¹-d¹ unit. In 4, paramagnetism is consistent with four V(III) ions. The V-V distance of 2.876 Å and electron count imply a formal bond order of 2/3. Both reactions resulted in desulfurization of dithioacetic acid, vanadocene reacted to yield only partial desulfurization upon formation of 4.

As discussed above, the V-V bond distance in 3 is 2.800(2) Å and is nearly the same as the V-V bond distance in the tightly bound V(μ - η^2 -S₂)₂V⁺ unit (V-V distance of 2.83 Å [18]) in the mineral patronite, (VS₄)_n and is similar to a recently described V-V compound prepared from VS₄³⁻ and a dithiuram disulfide derivative (V-V distance of 2.85 Å [19]). The stability of the V₂S₄ core in 3 is evidenced by the identification of V₂S₄⁺ in the mass spectrum (70 eV, solid probe). The cubic unit in 4 represents the first structure of the V parent compound in the cubic cyclopentadienyl-metal sulfide cluster series [11], the methyl-cyclopentadienyl complex being previously characterized [20]. Finally, the difference in chemistry between (η^6 -C₆H₆)₂V and (η^5 -C₅H₅)₂V illustrates the potential utility of V(0) starting materials to explore new metal-sulfide chemistry; the chemistry of cyclopentadienyl metal-sulfur compounds is well established [11].

CONCLUSIONS

We and others [13, 19, 20] have shown that the chemistry of early transition metals is similar to that of later transition metals [7-11] in the formation of sulfide metal complexes. While the strong metal-sulfur bond and related electronic factors preclude useful HDS catalysis activity of early transition metal sulfides, the fact that vanadium is present in relatively high concentration in crude oil argues for the study of vanadium and heteronuclear-vanadium sulfide systems. The vanadium dimer 3, represents an easily-prepared model complex of a mineral of relevance to HDS catalysis. The use of low-valent π -bonded sandwich compounds and dithiocarboxylic acids as starting materials to prepare metal sulfur-containing complexes is novel and shows the potential for the development of facile syntheses of new early transition metal sulfide compounds. More importantly this chemistry may be useful for producing mixed metal sulfide complexes, more likely to be useful as models of or precursors to catalytic species [21]. We are currently extending our work in this direction.

ACKNOWLEDGEMENTS

S.A.D. and M.T.A. acknowledge support from the Petroleum Research Fund, a Research Creative Activity Award (Cleveland State University) and a Research Challenge Grant (Ohio Board of Regents). S.A.D. acknowledges partial support from NASA grant NCC 3-162. A.F.H. acknowledges support from the Director's Discretionary Fund at NASA Lewis. We thank Dr. P. Kibala and Prof. F.A. Cotton, Texas A&M University, for x-ray structural analysis of 3.

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- [14] Crystal Structure Data for 1: Space Group, $Pcba$; $a = 16.964(5)$ Å, $b = 24.545(10)$ Å, $c = 7.832(2)$ Å, $Z = 8$, and $V = 3261(9)$ Å³.
- [15] Crystal Structure Data for 2: Space Group, $P2_1/c$; $a = 13.365(2)$ Å, $b = 7.906(4)$ Å, $c = 13.710(2)$ Å, $\beta = 96.44(3)^\circ$, $Z = 4$, and $V = 1440(1)$ Å³.
- [16] Crystal Structure Data for 3: Space Group, $P2_1/c$; $a = 10.425(2)$ Å, $b = 11.123(2)$ Å, $c = 9.133(4)$ Å, $\beta = 97.12(2)^\circ$, $Z = 2$, and $V = 1051(1)$ Å³.
- [17] Crystal Structure Data for 4: Space Group, $C2/c$; $a = 17.764(5)$ Å, $b = 8.119(2)$ Å, $c = 16.158(2)$ Å, $\beta = 116.65(2)^\circ$, $Z = 4$, and $V = 2083(2)$ Å³.
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1. Report No. NASA TM-103666		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle Reactivity of π -Complexes of Ti, V, and Nb Towards Dithioacetic Acid: Synthesis and Structure of Novel Metal Sulfur-Containing Complexes				5. Report Date	
				6. Performing Organization Code	
7. Author(s) Stan A. Duraj, Maria T. Andras, and Aloysius F. Hepp				8. Performing Organization Report No. E-5873	
				10. Work Unit No. 307-51-00	
9. Performing Organization Name and Address National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135-3191				11. Contract or Grant No.	
				13. Type of Report and Period Covered Technical Memorandum	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546-0001				14. Sponsoring Agency Code	
15. Supplementary Notes Prepared for the Fall Meeting of the Materials Research Society, Boston, Massachusetts, November 26— December 1, 1990. Stan A. Duraj and Maria T. Andras, Cleveland State University, Cleveland, Ohio.					
16. Abstract In order to use sulfur-containing resources economically and with minimal environmental damage, it is important to understand desulfurization processes. Hydrodesulfurization, for example, is carried out on the surface of a heterogeneous metal sulfide catalyst. Studies of simple, soluble inorganic systems provide information regarding the structure and reactivity of sulfur-containing compounds with metal complexes. Further, consistent with recent trends in materials chemistry, many model compounds warrant further study as catalyst precursors. We describe the reactivity of low-valent organometallic sandwich π -complexes towards dithiocarboxylic acids. For example, treatment of bisbenzene vanadium with CH_3CSSH affords a novel divanadium tetrakis(dithioacetate) complex. The crystallographically determined V-V bond distance, 2.800(2), is nearly the same as the V-V bond distance in a $\text{V}(\mu\text{-}\eta^2\text{-S}_2)_2\text{V}'$ unit in the mineral patronite, $(\text{VS}_4)_n$. The stability of the V_2S_4 core in the dimer is demonstrated by evidence of V_2S_4^+ in the mass spectrum (70 eV, solid probe) of the vanadium dimer. Several other systems relevant to HDS catalysis are also discussed.					
17. Key Words (Suggested by Author(s)) Catalysts; Metal sulfides; Nb sandwich compounds; V sandwich compounds; Organometallic sulfides			18. Distribution Statement Unclassified - Unlimited Subject Category 25		
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No. of pages 5	
				22. Price* A02	

